

CLAIMS

1. A production method for producing Group-III-element nitride single crystals comprising:
 - 5 heating a reaction vessel containing at least one metal element selected from the group consisting of an alkali metal and an alkaline-earth metal and at least one Group III element selected from gallium (Ga), aluminum (Al), and indium (In) to prepare a flux of the metal element; and feeding nitrogen-containing gas into the reaction vessel and thereby
 - 10 allowing the at least one Group III element and nitrogen to react with each other in the flux to grow Group-III-element nitride single crystals, wherein the Group-III-element nitride single crystals are grown, with the flux and the at least one Group III element having been stirred to be mixed together.
- 15 2. The production method according to claim 1, wherein the reaction vessel is rocked and thereby the flux and the at least one Group III element are stirred to be mixed together.
- 20 3. The production method according to claim 2, wherein the reaction vessel is rotated instead of or in addition to being rocked.
4. The production method according to claim 2, wherein a substrate is placed in the reaction vessel, a thin film of Group-III-element nitride is formed on a surface of the substrate beforehand, and Group-III-element nitride single crystals are grown on the thin film.
- 25 5. The production method according to claim 4, wherein the single crystals are grown with a liquid mixture of the flux containing the at least one Group III element and the at least one Group III element flowing

continuously or intermittently in a thin layer state on a surface of the thin film formed on the substrate.

6. The production method according to claim 4, wherein before the
5 Group-III-element nitride single crystals start growing, the reaction vessel is tilted in one direction, so that a liquid mixture of the flux and the at least one Group III element is pooled on a bottom of the reaction vessel on a side to which the reaction vessel is tilted and thereby the liquid mixture is prevented from coming into contact with a surface of the thin film of the substrate.

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7. The production method according to claim 4, wherein after the Group-III-element nitride single crystals finish growing, the reaction vessel is tilted in one direction, so that a liquid mixture of the flux and the at least one Group III element is removed from a surface of the thin film of the substrate
15 and is pooled on a side to which the reaction vessel is tilted.

8. The production method according to claim 1, wherein the flux and the at least one Group III element are stirred to be mixed together by heating a lower part of the reaction vessel to generate heat convection in addition to the
20 heating of the reaction vessel for preparing the flux.

9. The production method according to claim 1, wherein the at least one Group III element is supplied to the flux while the Group-III-element nitride single crystals grow.

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10. The production method according to claim 1, wherein the at least one Group III element is gallium (Ga), and the Group-III-element nitride single crystals are gallium (Ga) nitride single crystals.

11. The production method according to claim 1, wherein the alkali metal
30 is at least one selected from the group consisting of lithium (Li), sodium (Na),

potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) while the alkaline-earth metal is at least one selected from the group consisting of calcium (Ca), strontium (Sr), barium (Br), and radium (Ra).

5 12. The production method according to claim 1, wherein the flux of the at least one metal element is a sodium flux.

13. The production method according to claim 1, wherein the flux of the at least one metal element is a mixed flux of sodium and calcium.

10 14. The production method according to claim 13, wherein the ratio of the calcium (Ca) to the sum of the sodium (Na) and the calcium (Ca) is in a range of 0.1 mol% to 99 mol%.

15 15. The production method according to claim 1, wherein the mixed flux is a mixed flux of sodium (Na) and lithium (Li).

16. The production method according to claim 15, wherein the ratio of the lithium (Li) to the sum of the sodium (Na) and the lithium (Li) is in a range of 20 0.1 mol% to 99 mol%.

17. The production method according to claim 1, wherein the at least one Group III element and nitrogen react with each other under conditions including a temperature of 100°C to 1200°C and a pressure of 100 Pa to 25 20 MPa.

18. The production method according to claim 1, wherein the nitrogen(N)-containing gas is at least one of nitrogen (N₂) gas and ammonia (NH₃) gas.

19. The production method according to claim 1, wherein the nitrogen(N)-containing gas is ammonia (NH₃) gas or a mixed gas of ammonia (NH₃) gas and nitrogen (N₂) gas.

5 20. The production method according to claim 4, wherein the thin film formed on the substrate is single crystals of Group-III-element nitride or is amorphous Group-III-element nitride.

10 21. The production method according to claim 4, wherein the largest diameter of the thin film formed on the substrate is at least 2 cm.

22. The production method according to claim 4, wherein the largest diameter of the thin film formed on the substrate is at least 3 cm.

15 23. The production method according to claim 4, wherein the largest diameter of the thin film formed on the substrate is at least 5 cm.

20 24. The production method according to claim 1, wherein impurities that are intended to be used for doping are allowed to be present in a liquid mixture of the flux and the at least one Group III element.

25 25. The production method according to claim 24, wherein the impurities are at least one selected from the group consisting of calcium (Ca), a compound containing calcium (Ca), silicon (Si), alumina (Al₂O₃), indium (In), aluminum (Al), indium nitride (InN), silicon nitride (Si₃N₄), silicon oxide (SiO₂), indium oxide (In₂O₃), zinc (Zn), magnesium (Mg), zinc oxide (ZnO), magnesium oxide (MgO), and germanium (Ge).

30 26. The production method according to claim 1, wherein transparent single crystals are grown.

27. The production method according to claim 1, wherein the flux and the at least one Group III element are stirred to be mixed together, which is carried out in an atmosphere of inert gas other than nitrogen first and then 5 in an atmosphere of the nitrogen-containing gas that is obtained by substituting the inert gas by the nitrogen-containing gas.

28. The production method according to claim 27, wherein the inert gas is substituted by the nitrogen-containing gas gradually.

10 29. The production method according to claim 1, wherein the flux and the at least one Group III element are stirred to be mixed together using a stirring blade.

15 30. The production method according to claim 29, wherein the flux and the at least one Group III element are stirred to be mixed together using the stirring blade, which is carried out through a rotational motion or a reciprocating motion of the stirring blade or a combination thereof.

20 31. The production method according to claim 29, wherein the flux and the at least one Group III element are stirred to be mixed together using the stirring blade, which is carried out through a rotational motion or a reciprocating motion of the reaction vessel with respect to the stirring blade or a combination thereof.

25 32. The production method according to claim 29, wherein the stirring blade is formed of at least one material selected from:
(A) a material that is free from nitrogen and has a melting point or a decomposition temperature of at least 2000°C; and
(B) at least one material selected from the group consisting of rare

earth oxide, alkaline-earth metal oxide, W, SiC, diamond, and diamond-like carbon.

33. The production method according to claim 29, wherein the stirring 5 blade is formed of at least one material selected from the group consisting of Y_2O_3 , CaO, MgO, and W.

34. The production method according to claim 32, wherein the at least one material is Y_2O_3 .

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35. The production method according to claim 1, wherein the reaction vessel is a crucible.

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36. Transparent Group-III-element nitride single crystals obtained by a production method according to claim 1.

37. An apparatus that is used in a production method for producing Group-III-element nitride single crystals according to claim 2, comprising:

20 a means for heating a reaction vessel for preparing a flux by heating at least one metal element selected from the group consisting of an alkali metal and an alkaline-earth metal contained in the reaction vessel;

a means for feeding nitrogen-containing gas to be used for reacting a Group III element contained in the flux and nitrogen to each other by feeding the nitrogen-containing gas into the reaction vessel; and

25 a means for rocking the reaction vessel in a certain direction, wherein the means tilts the reaction vessel in one direction and then tilts it in an opposite direction to the one direction.

38. The apparatus according to claim 37, wherein the reaction vessel is a 30 crucible.

39. A reaction vessel that is used in a production method for producing Group-III-element nitride single crystals according to claim 2,

5 wherein the reaction vessel has a cylindrical shape and includes two projections that protrude from an inner wall thereof toward the circular center, and a substrate placed between the two projections.

40. The reaction vessel according to claim 39, wherein the reaction vessel is a crucible.

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41. A reaction vessel that is used in a production method for producing Group-III-element nitride single crystals according to claim 2,

15 wherein the reaction vessel is formed of or coated with at least one material selected from the group consisting of AlN, SiC, and a carbon-based material.

42. The reaction vessel according to claim 41, wherein the reaction vessel is a crucible.

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43. A semiconductor device comprising transparent Group-III-element nitride single crystals according to claim 36.

44. The semiconductor device according to claim 43, comprising a semiconductor layer,

25 wherein the semiconductor layer is formed of the transparent Group-III-element nitride single crystals according to claim 36.

45. The semiconductor device according to claim 44, comprising a field-effect transistor element in which a conductive semiconductor layer is 30 formed on an insulating semiconductor layer, and a source electrode, a gate

electrode, and a drain electrode are formed thereon,

wherein at least one of the insulating semiconductor layer and the conductive semiconductor layer is formed of transparent Group-III-element nitride single crystals according to claim 36.

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46. The semiconductor device according to claim 45, further comprising a substrate,

wherein the field-effect transistor element is formed on the substrate, and the substrate is formed of transparent Group-III-element nitride single 10 crystals according to claim 36.

47. A semiconductor device comprising a light-emitting diode (LED) element including an n-type semiconductor layer, an active region layer, and a p-type semiconductor layer that are stacked together in this order,

15 wherein at least one of the n-type semiconductor layer, the active region layer, and the p-type semiconductor layer is formed of transparent Group-III-element nitride single crystals according to claim 36.

48. The semiconductor device according to claim 47, further comprising a 20 substrate,

wherein the light-emitting diode element is formed on the substrate, and the substrate is formed of transparent Group-III-element nitride single crystals according to claim 36.

25 49. A semiconductor device comprising a laser diode (LD) element including an n-type semiconductor layer, an active region layer, and a p-type semiconductor layer that are stacked together in this order,

wherein at least one of the n-type semiconductor layer, the active region layer, and the p-type semiconductor layer is formed of transparent 30 Group-III-element nitride single crystals according to claim 36.

50. The semiconductor device according to claim 49, further comprising a substrate,

5 wherein the laser diode element is formed on the substrate, and the substrate is formed of transparent Group-III-element nitride single crystals according to claim 36.